Cyclopropanation of Alkenes with Diazoeosters Using Cu@FeNPs

Significance: Copper-plated iron nanoparticles (Cu@FeNPs) catalyzed the cyclopropanation of alkenes with diazoesters to give the corresponding substituted cyclopropanes in up to 76% yield (16 examples). In the reaction of 4-vinylanisole with benzyl diazoacetate, the catalyst was recovered by magnetic separation and reused four times without significant loss of catalytic activity.

Comment: The authors reported previously the preparation of Cu@FeNPs and its application to the Huisgen reaction (Green Chem. 2012, 14, 622). ICP analysis revealed that 12 ppm of copper leached out from the fresh catalyst during the reaction. The leached copper species showed no catalytic activity.
Chemoselective Reduction of α,β-Unsaturated Aldehydes with AuNPore

\[
\begin{align*}
\text{AuNPore (2 mol\% Au)} &\quad \text{TESH (3 equiv)} \\
&\quad \text{H}_2\text{O (6 equiv)} \\
&\quad \text{Et}_3\text{N (5 equiv)} \\
&\quad \text{MeCN, 70 °C, 24 h}
\end{align*}
\]

Results:

- 73% yield, \(2/3 > 99:1\)
- 70% yield, \(2/3 = 100:0\)
- 71% yield, \(2/3 = 89:11\)
- 78% yield, \(2/3 = 91:9\)
- 70% yield, \(2/3 = 91:9\)
- 70% yield, \(2/3 = 82:18\)
- 75% yield, \(2/3 = 100:0\)
- 70% yield, \(2/3 > 99:1\)
- X = Br, 45% yield, \(2/3 = 100:0\)
- X = F, 42% yield, \(2/3 = 100:0\)
- 46% yield, \(2/3 > 99:1\)
- 69% yield, \(2/3 > 99:1\)
- 62% yield, \(2/3 = 97:3\)

Significance: Nanoporous gold (AuNPore) catalyzed the 1,2-reduction of α,β-unsaturated aldehydes 1 with triethylsilane. The reduction was carried out in the presence of water and triethylamine to give the corresponding allyl alcohols 2 in 42–78% yield with 82:18 to 100:0 \(2/3\) chemoselectivity.

Comment: Previously, the authors reported the AuNPore-catalyzed chemoselective reduction of imines with dimethylphenylsilane (Org. Lett. 2014, 16, 2558). In the reduction of cinnamyl aldehyde, the catalytic activity of AuNPore was superior to that of Au30Ag70 alloy, homogeneous AuCl(Ph3P)/Bu3P, and AuCl/IPr·HCl. ICP-MS analysis showed that no gold content was leached from the catalyst during the reaction.
A Zeolitic Imidazolate Framework Catalyst for [3+3] Cycloadditions

**Significance:** The authors developed a hollow-structured zeolitic imidazolate framework (ZIF-8-H) nanosphere as a catalyst for [3+3] cycloadditions. ZIF-8-H was prepared via complexation of carboxylic groups on the surface of nano-PS (ø = 400 nm) with zinc ions and 2-methylimidazole, followed by subsequent removal of the PS nanosphere by extraction with toluene. The reaction of 1,3-dicarbonyl compounds 1 with α,β-unsaturated aldehydes 2 proceeded in the presence of ZIF-8-H to give the pyranyl heterocycles 3 with up to 89.0% conversion and 99.9% selectivity.

**Comment:** The reaction of 1,3-hexanedione and 3-methyl-2-butenal proceeded in the presence of ZIF-8-H with 89.0% conversion, whereas the use of bulk ZIF-8 showed lower catalytic efficiency (73.2% conversion). Toluene vapor adsorption isotherm showed that ZIF-8-H absorbed toluene to a cage-filling level with a high adsorption amount (6.34 mmol/g). Based on this observation, the authors discussed that the limiting aperture size of ZIF-8-H exceeded the kinetic diameter of toluene (0.61 nm), which is much larger than the reported window size of ZIF-8 (0.34 nm).
J. M. Pérez, D. J. Ramón* (Universidad de Alicante, Spain)

Cobalt-Impregnated Magnetite as General Heterogeneous Catalyst for the Hydroacylation Reaction of Azodicarboxylates


Hydroacylation of Azodicarboxylates with Aldehydes Using CoO–Fe₃O₄

**Significance:** Magnetite-supported cobalt oxide (CoO–Fe₃O₄) was prepared by mixing CoCl₂·6H₂O and Fe₃O₄ in water followed by treatment with NaOH (eq. 1). CoO–Fe₃O₄ catalyzed the hydroacylation of azodicarboxylates 1 with aldehydes 2 in trichloroethylene to afford the hydroacylated products 3 in up to 99% yield (eq. 2).

**Comment:** In the formation of 3a, the catalyst was recovered by magnetic separation and reused nine times with slight loss of its catalytic activity. The catalytic activity of CoO–Fe₃O₄ was superior to that of the other metal oxides supported on Fe₃O₄ (NiO–Fe₃O₄, CuO–Fe₃O₄, Ru₂O₃–Fe₃O₄, Rh₂O₃–Fe₃O₄, PdO–Fe₃O₄, Ag₂O/Ag–Fe₃O₄, WOₓ–Fe₃O₄, OsO–Fe₃O₄, PtO/PtO₂–Fe₃O₄, Au₂O₃/Au–Fe₃O₄, NiO/Cu–Fe₃O₄, PdO/Cu–Fe₃O₄) and unsupported CoO.

**Selected examples:**

- **3a** 89% yield
- **3b** 86% yield
- **3c** 67% yield
- **3d** 95% yield
- **3e** 87% yield
- **3f** 74% yield
- **3g** 99% yield
- **3h** 99% yield
A Heterogeneous Palladium Catalyst for C2-Selective Arylation of Indoles

**Significance:** Pd⁰-AmP-MCF constitutes of silica-based mesocellular foam (MCF) functionalized with aminopropylsilane (for the preparation, see: M. Shakeri et al. Chem. Eur. J. 2011, 17, 13269). Pd⁰-AmP-MCF (palladium particles ø: 2–3 nm) catalyzed the C2-selective arylation of indoles 1 and substituted diaryliodonium tetrafluoroborates 2 to give the corresponding indole derivatives in 65–99% yield (15 examples).

**Comment:** The reactions of an electron-rich indole (3b), an N-methylated indole (3d), para-alkyl-substituted salts (3f, g), or an electron-deficient CF₃-substituted salt (3j) afforded high yields, whereas an N-benzylated indole (3e) or a naphthyl salt (3i) resulted in lower yield. ICP-OES analysis showed 0.6 ppm of palladium leaching from the reaction mixture (3a).

**Selected results:**

<table>
<thead>
<tr>
<th>Compound</th>
<th>R¹</th>
<th>R²</th>
<th>Ar</th>
<th>Temperature</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>H</td>
<td>H</td>
<td>Ph</td>
<td>r.t., 6 h</td>
<td>91%</td>
</tr>
<tr>
<td>3b</td>
<td>MeO</td>
<td>H</td>
<td>Ph</td>
<td>40 °C, 6 h</td>
<td>86%</td>
</tr>
<tr>
<td>3c</td>
<td>NO₂</td>
<td>H</td>
<td>Ph</td>
<td>50 °C, 25 h</td>
<td>70%</td>
</tr>
<tr>
<td>3d</td>
<td>H</td>
<td>Me</td>
<td>Ph</td>
<td>r.t., 6 h</td>
<td>80%</td>
</tr>
<tr>
<td>3e</td>
<td>H</td>
<td>MeOH</td>
<td>Ph</td>
<td>50 °C, 24 h</td>
<td>65%</td>
</tr>
<tr>
<td>3f</td>
<td>H</td>
<td>Me</td>
<td>4-MeC₆H₄</td>
<td>40 °C, 6 h</td>
<td>83%</td>
</tr>
<tr>
<td>3g</td>
<td>H</td>
<td>H</td>
<td>4-t-BuC₆H₄</td>
<td>r.t., 15 h</td>
<td>84%</td>
</tr>
<tr>
<td>3h</td>
<td>H</td>
<td>H</td>
<td>2-MeC₆H₄</td>
<td>40 °C, 6 h</td>
<td>76%</td>
</tr>
<tr>
<td>3i</td>
<td>H</td>
<td>H</td>
<td>Np</td>
<td>40 °C, 15 h</td>
<td>67%</td>
</tr>
<tr>
<td>3j</td>
<td>H</td>
<td>Me</td>
<td>4-F₃CC₆H₄</td>
<td>40 °C, 6 h</td>
<td>99%</td>
</tr>
<tr>
<td>3k</td>
<td>H</td>
<td>Me</td>
<td>4-MeOC₆H₄</td>
<td>40 °C, 6 h</td>
<td>72%</td>
</tr>
</tbody>
</table>
C–H Borylation of Cyclopropanes and Cyclobutanes with Silica-SMAP–Iridium

**Significance:** The heteroatom-directed C–H borylation of cyclopropanes and cyclobutanes with bis(pinacolato)diboron was carried out in the presence of [Ir(OMe)(cod)]₂ and silica-SMAP to give the corresponding borylated products in up to 168% yield based on bis(pinacolato)diboron (eqs. 1 and 2).

**Comment:** In the reaction of 2-cyclopropylpyridine with bis(pinacolato)diboron, the catalytic activity of the silica-SMAP–iridium system was superior to that of the other ligand–iridium systems (for example, 0% yield for Ph-SMAP–Ir, Me₃P–Ir, t-Bu₃P–Ir, Ph₃P–Ir, XPhos–Ir, dtbpy–Ir, and 2,9-Me₂Phen–Ir).
Olefin Metathesis with Ruthenium–Carbene Supported on Iron Oxide

Significance: The Grubbs–Hoveyda ruthenium–carbene complex supported on ionic magnetic nanoparticles (Ru@IMNPs) was prepared by immobilization of imidazolium chloride 1 onto Fe$_3$O$_4$, anion exchange with NaPF$_6$, and metathesis with ruthenium complex 3 (eq. 1). Ru@IMNPs catalyzed the ring-closing metathesis of dienes to give the corresponding cyclic olefins in 90–99% yield (eq. 2). The cross-metathesis of methyl acrylate with olefins using Ru@IMNPs also proceeded with high $E$-selectivity (eq. 3).

Comment: In the ring-closing metathesis of $N,N$-diallyl tosylamide, the catalyst was recovered magnetically and reused five times without significant loss of catalytic activity (6th run: 96% conversion), although ICP-MS analysis showed significant leaching of the ruthenium species into the product (a loss of 54% of the ruthenium content of the fresh catalyst) during the initial three runs of the recycling experiment.
Hydroamination of Alkynes Using Amphiphiles-Based Au@SiO₂

Significance: The porous Au@SiO₂ catalyst was prepared from a gold precursor and a TEOS solution in the presence of cinchonidine-based triazole amphiphiles. The hydroamination of alkynes was carried out with Au@SiO₂ to give the corresponding imine products 1a–n in up to 99% conversion.

Comment: The turnover number of Au@SiO₂ was 1604 for the formation of 1b. The catalyst was characterized by cryo-TEM, XPS, UV/Vis, zeta potential, and ICP-OES analyses.

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Heterogeneous Copper-Catalyzed Cascade Three-Component Reaction of Amines, Carbon Disulfide and 2-Iodoanilines Leading to 2-Aminobenzothiazoles


Preparation of 2-Aminobenzothiazoles with an MCM-41-Cu Catalyst

Preparation of the MCM-41-supported copper complex catalyst:

\[
\text{CuCl}_{\text{DMF, r.t., 7 h}} \quad \text{OTMS} \quad \text{MCM-41-2N-CuCl}
\]

Selected results:

\[
\begin{align*}
1\text{a} & \quad R_1 = H, 95\% \text{ yield} \\
1\text{b} & \quad R_1 = 4-\text{Me}, 84\% \text{ yield} \\
1\text{c} & \quad R_1 = 4-\text{Cl}, 83\% \text{ yield} \\
1\text{d} & \quad R_1 = 4-\text{F}, 86\% \text{ yield} \\
1\text{e} & \quad R_1 = 4-\text{CF}_3, 85\% \text{ yield} \\
1\text{f} & \quad R_1 = H, 86\% \text{ yield} \\
1\text{g} & \quad R_1 = 4-\text{Me}, 79\% \text{ yield} \\
1\text{h} & \quad R_1 = 4-\text{Cl}, 80\% \text{ yield} \\
1\text{i} & \quad R_1 = 4-\text{F}, 84\% \text{ yield} \\
1\text{j} & \quad R_1 = 4-\text{CF}_3, 82\% \text{ yield} \\
1\text{k} & \quad R_1 = 4-\text{Me}, 93\% \text{ yield} \\
1\text{l} & \quad R_1 = 4-\text{CN}, 87\% \text{ yield} \\
1\text{m} & \quad 81\% \text{ yield} \\
1\text{n} & \quad 71\% \text{ yield} \\
1\text{o} & \quad 82\% \text{ yield} \\
1\text{p} & \quad 81\% \text{ yield} \\
1\text{q} & \quad 78\% \text{ yield}
\end{align*}
\]

Significance: The mesoporous catalyst MCM-41-2N-CuCl was prepared by immobilization of a 3-(2-aminoethylamino)propyl moiety on MCM-41 with CuCl. The reaction of 2-iodoanilines, carbon disulfide (CS₂) and amines with 10 mol% of MCM-41-2N-CuCl gave the corresponding 2-aminobenzothiazoles 1a–q in up to 95% yield.

Comment: The MCM-41-2N-CuCl catalyst was recovered by filtration and reused nine times to give 1a (5th reuse: 94% yield, 9th reuse: 93% yield). ICP-AES analysis revealed that no copper species leached into the reaction mixture.
Click Reaction Using Polymer-Supported Cul–Cryptand-22

**Significance:** A polystyrene resin supported Cul–cryptand-22 complex (PS–C22–CuI) was prepared by mixing chloromethylated polystyrene with cryptand-22 in diethyl ether, followed by the complexation with CuI in ethanol (eq. 1). PS–C22–CuI catalyzed the click reaction of azides with terminal alkynes (eq. 2, method A) or the one-pot three-component reaction from alkyl halides, sodium azide, and terminal alkynes (eq. 3, method B) to give the corresponding 1,2,3-triazoles in up to 99% yield.

**Comment:** The PS–C22–CuI complex was characterized by FT-IR, EDX, SEM, XPS, and TG-DTA analysis. In both methods A and B for synthesizing 1-benzyl-4-phenyl-1H-1,2,3-triazole, the catalyst was recovered by filtration and reused three times.

**Selected examples:**

99% yield (eq. 2) 99% yield (eq. 3, X = Br)
78% yield (eq. 2) 73% yield (eq. 3, X = Br)
93% yield (eq. 2) 85% yield (eq. 3, X = Br)
86% yield (eq. 2) 82% yield (eq. 3, X = Cl)
The Mizoroki–Heck Reaction Using a Palladium–NHC Complex Supported on MNP

**Significance:** A palladium–NHC complex was immobilized on magnetic nanoparticles (Pd–NHC@MNP) according to the sequences shown above. Pd–NHC@MNP catalyzed the Mizoroki–Heck reaction of terminal alkenes with aryl halides to afford the corresponding internal alkenes in up to 96% yield (eq. 2).

**Comment:** The characterization of Pd–NHC@MNP was performed by TEM, EDX, IR, TGA, DSC, $^1$H NMR spectroscopy, and ETAAS analyses. In the Mizoroki–Heck reaction of butyl acrylate with iodobenzene, the catalyst was recovered magnetically and reused four times without loss of its catalytic activity (1st run: 85% yield, 3rd run: 87% yield, 5th run: 85% yield).

**Selected results:**

- $\text{R}^1 = \text{Fe}_3\text{O}_4$ (1 equiv) + $X = \text{I}$ up to 96% yield (11 examples)
- $\text{R}^1 = \text{BuO}$ (1 equiv) + $X = \text{I}$ 96% yield
- $\text{R}^1 = \text{BuO}$ (1 equiv) + $X = \text{Br}$ 95% yield
- $\text{R}^1 = \text{BuO}$ (1 equiv) + $X = \text{I}$ 82% yield
- $\text{R}^1 = \text{BuO}$ (1 equiv) + $X = \text{I}$ 86% yield
- $\text{R}^1 = \text{BuO}$ (1 equiv) + $X = \text{Br}$ 72% yield
- $\text{R}^1 = \text{BuO}$ (1 equiv) + $X = \text{I}$ 48% yield
- $\text{R}^1 = \text{BuO}$ (1 equiv) + $X = \text{Br}$ 72% yield
- $\text{R}^1 = \text{BuO}$ (1 equiv) + $X = \text{Br}$ 72% yield
- $\text{R}^1 = \text{BuO}$ (1 equiv) + $X = \text{I}$ 94% yield
- $\text{R}^1 = \text{BuO}$ (1 equiv) + $X = \text{Br}$ 95% yield
- $\text{R}^1 = \text{BuO}$ (1 equiv) + $X = \text{Br}$ 72% yield
- $\text{R}^1 = \text{BuO}$ (1 equiv) + $X = \text{I}$ 94% yield
- $\text{R}^1 = \text{BuO}$ (1 equiv) + $X = \text{Br}$ 95% yield
- $\text{R}^1 = \text{BuO}$ (1 equiv) + $X = \text{Br}$ 72% yield
Visible-Light-Promoted aza-Henry Reaction Using Mesoporous Cu$_2$O

Significance: Mesoporous copper(I) oxide spheres with different pore sizes (5 nm for SP-Cu$_2$O and 15 nm for LP-Cu$_2$O) were prepared and applied to the visible-light-promoted aza-Henry reaction. The reaction of $N$-aryl tetrahydroisoquinolines 1 with nitroalkanes 2 was carried out in the presence of LP-Cu$_2$O and molecular oxygen under the irradiation of blue LEDs to afford the corresponding coupling products 3 in 83–90% yield. The reaction without catalyst gave 3a in only 5% yield under otherwise similar conditions.

Comment: The catalysts were characterized by SEM, TEM, XRD, and N$_2$ adsorption–desorption analyses. For the formation of 3a, LP-Cu$_2$O was recovered by centrifugation and reused four times without significant loss of catalytic activity. SEM observation of LP-Cu$_2$O after the fifth run showed no change of its morphology. The preparation of mesoporous Cu$_2$O spheres with small pore size was previously reported by Shang, Zhang and Guo (J. Mater. Chem. 2012, 22, 856).

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Asymmetric α-Benzylolation with Cinchonidium Salt Based Polymers

Significance: Chiral polymers 3 and 5 were prepared from cinchonidine dimers 1 (eqs. 1 and 2). All polymers showed high catalytic performance in the asymmetric α-benzylation of N-diphenylmethylene glycine tert-butyl ester with benzyl bromide (eq. 3, 77–95% yield, 81–92% ee).

Comment: The polymer catalysts were recovered by filtration and reused without loss of catalytic performance. The reaction also took place at –40 °C to give the product with improved ee (with 3bc: 24 h, 83% yield, 95% ee). The catalytic activity and the stereoselectivity observed with the polymeric catalysts 3 and 5 were comparable to those obtained with the homogeneous catalysts 1.
B. KARAMI,* M. FARAH, F. PAM (YASOUJ UNIVERSITY, IRAN)
A Green Protocol for the N-Formylation of Amines Using Molybdate Sulfuric Acid as a Reusable Solid Catalyst

**N-Formylation of Amines Using Molybdate Sulfuric Acid**

**Significance:** Molybdate sulfuric acid (MSA) catalyzed the N-formylation of amines with orthoformates to give the corresponding formamide derivatives in up to 95% yield (19 examples). In the N-formylation of aniline with triethyl orthoformate, the catalyst was recovered by filtration and reused three times with a slight loss of catalytic activity (1st reuse: 87% yield, 3rd reuse: 80% yield).

**Comment:** The catalytic activity of MSA was superior to that of the other catalysts (ZnO, ZrOCl₂, MgBr₂, ZnCl₂, and H₂SO₄). The authors have reported previously the preparation of molybdate sulfuric acid and its application to the synthesis of phenazines and quinoxalines (Polycycl. Aromat. Compd. 2011, 31, 97).

**Selected examples:**

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>Yield (R = Me)</th>
<th>Yield (R = Et)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>N</td>
<td>H</td>
<td>90%</td>
</tr>
<tr>
<td>OMe</td>
<td>N</td>
<td>95%</td>
<td>85%</td>
</tr>
<tr>
<td>NO₂</td>
<td></td>
<td>67%</td>
<td>70%</td>
</tr>
<tr>
<td>CH₃</td>
<td>N</td>
<td>87%</td>
<td>80%</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>80%</td>
<td>80%</td>
</tr>
<tr>
<td>OMe</td>
<td>N</td>
<td>65%</td>
<td>73%</td>
</tr>
</tbody>
</table>

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